X.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLIV. — THERMO–ELECTRIC INTERPOLATION FORMULÆ.

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In this paper are collected the several well known types of formulæ for expressing the thermal electro-motive force of a couple as a function of the temperature of its junctions. Two new formulæ are also proposed. All then are tested against the most reliable experimental data upon the subject, and their relative merits discussed.

The Existing Formulæ.

Consider a simple closed electric circuit composed of two different metals, each homogeneous in matter and temper, the metals being in contact at two points. For simplicity, assume the metals to be in the form of wires joined at their ends. Let one junction be at a temperature of $h°$, the other of $c°$, on the ordinary centigrade scale. Let $\Sigma_c^h e$ be employed as a suggestive symbol to denote the resultant electro-motive force in the circuit, induction being excluded from consideration. Then $\Sigma_c^h e$ is a function of h and c which involves constants dependent upon the nature of the metals, and which may be represented by

$$\Sigma_c^h e = f(h, c).$$

The discovery of the natural expression for $f(h, c)$ is not only of scientific importance, but is urgently needed in the development of the art of pyrometry. At present even a satisfactory empirical formula for interpolation is lacking, the best still being probably that of Avenarius and Tait.

The existing formulæ are the five following.

Ordinary or parabolic:

$$\Sigma_0^t e = a\, t + b\, t^2 + c\, t^3 + \; . \; . \; . \; . \; . \tag{1}$$

This is, of course, merely a series in ascending powers of t, where one junction is at any temperature t° C., and the other at 0° C., a, b, and c being constants. A more general form for the case where the cold junction is at any constant temperature, t_1°, is

$$\Sigma_{t_1}^t e = a\,(t - t_1) + b\,(t^2 - t_1^2) + c\,(t^3 - t_1^3) + \; . \; . \; . \; . \; .$$

These expressions may, of course, be inverted, giving t as a function of $\Sigma\, e$.

Avenarius

$$\Sigma_c^h e = (h - c)\,\{a + b\,(h + c)\}, \tag{2}$$

in accordance with the foregoing notation.

Thomson:

$$\Sigma_c^h e = a\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\}, \tag{3}$$

where τ is the absolute temperature, τ_n being that of the "neutral point."

Tait:

$$\Sigma_0^h e = (k' - k)\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\}. \tag{4}$$

Both of the last two, by the substitution of $t + 273$ for τ obviously reduce to the Avenarius form.

Barus:

$$e_h + e_e = 10^{\,P + Qh} + 10^{\,P' + Q'c,} \tag{5}$$

where e_h represents the thermal emf. of the hot junction and e_c that of the cold junction. In view, however, of the existence of the Thomson effect, these symbols can strictly be interpreted only as having the meaning that $e_h - e_c = \Sigma_c^h e$.

Note. — With regard to the Avenarius, Thomson, and Tait expressions it may be remarked that they are not only mutually equivalent, but that if t_c or τ_c becomes 0° C. they reduce at once to the ordinary parabolic form of two terms:

$$\Sigma_0^t = a\, t + b\, t^2.$$

They are all, therefore, forms which must apply if the latter purely empirical expression for the same temperature ranges applies, and with the same closeness, so that it is unnecessary to test more than

one of the first four expressions against any one set of data. Also the fact that the Avenarius and Tait equations approximately conform to the observed data does not necessarily in any material degree strengthen the hypotheses which are adduced to show that these equations are a natural expression of the law.

Without attempting here a further analysis of the components making up the resultant emf. $\Sigma_c^h e$, which is the measured emf. of the thermo-couple, the proposed interpolation formulæ will be merely developed and applied. It may, however, be suggested in passing, that there seems to the writer to be little hope of arriving at a close approximation to the natural law except through an expression which shall contain separate terms representing the temperature function of the component arising at the contact of the dissimilar metals, and that arising from the inequality of temperature of the ends of each (homogeneous) element (Thomson emf.). The parabolic and Avenarius formulæ would comply in part with this requirement on the supposition that the emf. at contact varied as the first power, and the Thomson emf. in both wires as the square of the temperature. And looked at from that point of view, the neutral point would seem to have an explanation materially different from that usually accorded to it.

The Proposed Formulæ.

Exponential Equation. — The significance of this proposed expression may be thus stated. Suppose the cold junction of the couple be maintained at the absolute zero of temperature, $\tau = 0°$, and its emf. to be consequently zero. Let the other (hot) junction be at any temperature τ_h^o absolute. The proposed equation is based on the assumption that the total emf. of the couple would then be representable by

$$e' = m\,\tau_h^n.$$

where m and n are numerical constants. If then the cold junction were raised to any temperature τ_c^o there would be introduced an opposing emf. e'', which would be expressible by

$$e'' = m\,\tau_c^n.$$

The resultant emf. $\Sigma_c^h e$ would then be $e' - e''$, and therefore expressible by

$$\Sigma_c^h e = m\,\tau_h^n - m\,\tau_c^n. \tag{6}$$

If in any instance, as is frequently the case in measurements, the temperature of the cold junction is maintained constant while that of the

hot junction varies, then $m \tau_c^n$ becomes a constant, and it will be convenient to denote this constant by β when $\tau = 273°$ abs. $= 0°$ C. So that for this special case where the cold junction is at $0°$ C. and the hot junction at $t°$ C., we have

$$\Sigma_0^t e = m \tau^n - \beta. \qquad (7)$$

This expression is not advanced as a possible natural form of the function $f\,(h,c)$. It is essentially empirical, and is not designed to account separately for the several distinct components entering into Σe. The fact that it closely fits the experimental data arises chiefly from the well known adaptability of the exponential equation to represent limited portions of curved lines. The equation also leads to certain inferences which appear inconsistent with the known thermo-electric laws, and fails to explain some known phenomena.

The evaluation of the constants m, n, and β is unfortunately attended by considerable labor. No application of the method of least squares readily presents itself, but by a method of successive approximations the values can be obtained with any desired degree of exactitude. Only two measured pairs of values of $\Sigma_0^t e$ and t are necessary for this approximation method, the third required pair being furnished by $\Sigma_0^0 e = 0$ and $t = 0$; although, of course, by the employment of three pairs of values well distributed in the data, a more closely fitting equation might frequently be obtained. The calibration of a thermo-couple for pyrometric work can thus be affected by the employment of but two known temperatures, and this, on account of the uncertainty of our knowledge of high melting points, is of great importance in high temperature work.

Let $t_0 = 0°$ C., t', and t'' be the selected observed temperatures from which to compute the constant, so that $\tau_0 = 273°$, $\tau' = t' + 273°$, $\tau'' = t'' + 273°$ abs. And let $\Sigma_0^{t_0} e = 0$, $\Sigma_0^{t'} e$, $\Sigma_0^{t''} e$, be the corresponding observed emfs. of the couple. Then, by substituting these in equation (7), and combining the three expressions, or their logarithms, we easily deduce

$$\beta = \frac{\Sigma_0^{t'} e}{\left(\dfrac{\tau'}{\tau_0}\right)^n - 1}; \qquad (8)$$

$$n = \frac{\log\,(\Sigma_0^{t''} e + \beta) - \log\,(\Sigma_0^{t'} e + \beta)}{\log \tau'' - \log \tau'}; \qquad (9)$$

$$m = \frac{\Sigma_0^{t''} e + \beta}{(\tau'')^n} \quad \text{or} \quad \frac{\Sigma_0^{t'} e + \beta}{(\tau')^n}. \qquad (10)$$

By means of these the numerical values of the constants may be calculated from those of τ', τ'', $\Sigma_0^{t'} e$, etc., as follows : —

1. Assume as a first approximation some value of n, say $n = 1$, unless some better approximation is in some way suggested. Substituting this value in (8), compute the corresponding value of β.

2. Using this as a first approximation, substitute it in (9) and compute the corresponding value of n.

3. Using this value as a second approximation to n, insert it in (8), and compute a second approximation to β.

4. With this compute a third approximation to n, and so continue until consistent values of β and n are found to the desired number of figures. Then compute m by (10).

The rate of convergence is not rapid, but after one or two approximations have been made an inspection of the rate will enable the computer to estimate values of n which will be nearer than the preceding approximation, and thus hasten the computation.

Where an equation is to be computed to best represent a progressive series of observed values of t and Σe, this method is of course open to some objections, since it incorporates in the constants the accidental errors of the selected observations from which the constants are deduced. This difficulty can be sufficiently overcome by computing residuals between the equation and the data, and amending the equation if necessary to give them a better distribution.

Logarithmic Formula. — A very simple expression for interpolation is of the general form

$$\Sigma_0^t e = m\, t^n,$$

where m and n are constants. This serves fairly well for a short range, $t'' - t'$, when $t' - 0°$ is not less than one third of $t'' - t'$.

The convenience of the expression arises from two facts: first, that its two constants are very easily evaluated either by computation or graphically from the logarithmic expression (whence the name)

$$\log \Sigma_0^t e = n \log t + \log m ;$$

second, that its logarithmic plot is a straight line, since this expression is the equation to a straight line if we regard $\log \Sigma_0^t e$ and $\log t$ as the variables. If, therefore, a series of values of Σe and t are known for a given couple, points obtained by plotting $\log t$ as abscissas and $\log \Sigma e$ as ordinates should lie along a straight line. Thus a couple may be completely " calibrated " for all temperatures by measuring Σe and t for any two values of t (suitably disposed). The constants m and n

may be computed, or a plot of log $\Sigma\,e$ and log t may be made, and a straight line be drawn through them. Graphical interpolation on this line will then of course yield the values of log t and hence of t corresponding to observed values of $\Sigma\,e$, and *vice versa*, and, if desired, the constants m and n. The expression for t as a function of $\Sigma\,e$ is, of course,

$$t = m'\,(\Sigma_0^t\,e)^{n'}, \quad \text{or} \quad t = \left(\frac{\Sigma_0^t\,e}{m}\right)^{\frac{1}{n}}.$$

This formula is well adapted to pyrometric work not of the very highest grade of accuracy, and has been advantageously employed in connection with the Le Chatelier thermo-electric pyrometer in a method to be described in a later article.

TEST OF FORMULÆ.

This will be made by applying the several formulæ to the experimental data of Barus, Holborn and Wien, Chassagny and Abraham, and Noll. These investigators employed modern methods of thermometry and of electrical measurement. Temperatures are either made in or reduced to the scale of the hydrogen (C. & A.), or of the air thermometer (B., H. & W., N.). Constants for the formulæ will be deduced, and the residuals or deviations of the data from the equations (i. e. δ = data-equation) will be computed for the observed points. For discussion these deviations will be expressed in percentages, viz. $100\,\frac{\delta}{e}$, rather than in microvolts or degrees. This is preferable because the process of measurement of the emf., and to some extent at least of the temperature, is such as to yield results of a nearly constant fractional or percentage precision at all temperatures rather than of a constant number of microvolts or degrees. Thus by comparing percentages we eliminate a complication arising otherwise from the increasing value of δ as t increases. Incidentally there are also other well recognized advantages frequently attending the comparison of percentages rather than of absolute quantities.

The Barus Data. — Taking the data in the order of priority, those of Barus will be first employed. The measurements to be used consist of very elaborate and painstaking direct comparisons of several 20 per cent irido-platinum thermo-couples with several porcelain bulb air thermometers used under the constant pressure method.

Quotations of, or rather interpolations in, his original data * are

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* Barus, C.   U. S. Geol. Surv. Bull., No. 54 (1889).   Phil. Mag., XXXIV. 1 (1892).

given by Barus * later, as a basis from which to deduce constants for his proposed equation

$$e + e_0 = 10^{\,P + Qh} + 10^{\,P' + Q'c}.$$

Barus's numerical values for the constants are :

$$e_0 = 45680 \text{ microvolts.}$$

$$P = 4.6515 \text{ `` } \qquad Q = 1.106 \cdot 10^{-4}.$$

$$P' = 2.849 \text{ `` } \qquad Q' = 3.01 \cdot 10^{-3}.$$

These constitute his "equation 3," for which e_0 corresponds to 20° C. The data and the deviations which I have computed for it, viz. $\delta =$ data-equation, are given in Table I. The last column gives the deviations expressed in percentages, viz. $100\,\frac{\delta}{E}$, where $E = e + e_0 + 1880$. This value of E is adopted to make the percentages comparable with those in subsequent discussions. The number 1880 is $1730 + 150$, which are the values of e_0 and $\Sigma_0^{20}\,e$ of the next two pages.

TABLE I.

BARUS'S AMERICAN JOURNAL OF SCIENCE DATA.

t^0	$e + e_0$ mv. Observed.	$e + e_0$ Computed from " Equ. 3."	δ mv.	$100\frac{\delta}{E}$ Per Cent.
° C.				
0	−150			
100	+680	653	+27	+1.11
200	1650	1657	−7	−0.20
300	2760	2788	−28	−0.60
400	3950	3994	−44	−0.80
600	6560	6551	+9	+0.11
800	9310	9273	+37	+0.34
1000	12200	12140	+60	+0.43

The lines AB and CD on the diagram (page 212), constructed with percentage deviations as ordinates and temperatures as abscissas show clearly that the deviations are systematic. Upon inspection of this plot

* Amer. Jour. Sci., XLVIII. 332 (1894). See also XLVII. 366 (1894).

it appears that the data may be separated into two groups, one includ-
ing 0°–300° ; the other 400°–1000°, which appear to have entirely
distinct forms of systematic error. This division corresponds to two
distinct groups of data, one extending from 0° to 300°, the other
including the second group and extending from 350° to 1075°. The
latter were given in the Bulletin as the final results of the high tem-
perature comparisons of the irido-platinum couple with porcelain bulb
air thermometers. The detailed statement of the 0°–300° comparison
I have not seen. Although the discrepancy between the two sets of
systematic deviations is not extremely large, yet it has seemed to me
that it was beyond the limits of concordance in the higher tempera-
ture work, and that it would be better for the present purpose to deal
solely with the 350°–1075° data. Two points regarding Barus's work
should be noticed : one the strikingly high degree of concordance be-
tween individual observations even with different thermometer bulbs
and different thermo-couples ; the other the remark in which Barus
notes a possibility of being able still further to reduce the " stem
error " entering into the result, which so far as I am aware has not
yet been done.

The high temperature air thermometer comparisons (Bulletin,
Series I., II., III., IV., and V.) of Barus are so numerous (108) and
so distributed that the labor of utilizing them simply for deducing con-
stants and testing an equation would be excessive. Also they are too
concordant to permit interpolation on a direct plot without a sacrifice
of some of their precision. For the purposes of discussion, therefore,
I averaged them in nine groups. The first group contained all where
the emf. lay between 3,000 and 4,000 microvolts ; the second group
between 4,000 and 5,000 mv. ; and so on by steps of 1,000 microvolts,
except that the seventh group covered 2,000 mv. from 9,000 to 11,000.
These groups were not exactly equal in number of observations, and
therefore in weight, nor is the arithmetical average a strictly legiti-
mate value where the function is not linear; but, as easily seen by
inspection of the originals, the errors thus introduced are negligible.
In Table II., columns one and two give the direct values of the
averages. Column three reduces $\Sigma_{20}^{t} e$ to $\Sigma_{0}^{t} e$ by adding 150 micro-
volts the value of $\Sigma_{20}^{0} e$ being elsewhere given by Barus as —150
microvolts.

TABLE II.

BARUS'S AIR THERMOMETER COMPARISONS, SERIES I.–V.

t^0	$\Sigma_{20}^t e$	$\Sigma_0^t e$	Avenarius.		Exponential.		Logarithmic.	
			δ Data Eq.	Per Cent $=100\frac{\delta}{e}$	δ Data Eq.	Per Cent $=100\frac{\delta}{e}$	δ Data Eq.	Per Cent $=100\frac{\delta}{e}$
° C.	mv.	mv.	mv.		mv.		mv.	
0.0	(−150)	0	0	0.0	+23	+1.3		
378.5	3679	3829	−84	−4.0	−66	−1.2	−33	−0.60
440.3	4508	4658	+18	+0.28	+18	+0.28	+30	+0.47
522.0	5486	5636	−4	−0.07	−25	−0.34	−36	−0.50
588.4	6404	6554	+70	+1.1	+33	+0.40	+9	+0.12
672.1	7550	7700	+110	+1.5	+60	+0.64	+26	+0.28
745.6	8530	8680	+82	+0.92	+26	+0.25	−9	−0.10
840.1	9898	10048	+101	+1.0	+49	+0.41	+26	+0.22
946.6	11396	11546	+9	+0.07	−19	−0.14	−13	−0.10
1019.7	12475	12625	−45	−0.32	−45	−0.32	−10	−0.07
Average percentage deviations . .				0.93		0.53		

The Avenarius equation applied to these data yields
$$\Sigma_0^t e = 9.104\, t + 3.249 \cdot 10^{-3}\, t^2.$$
Microvolts.   Range 350° to 1075° C.

Computing from this equation values of $\Sigma_0^t e$ for the successive values of t in column one, and subtracting them from the data in column three gives the deviations between data and equation. These are expressed in microvolts in column four, and in percentages in column five, the percentage being reckoned in terms of e_t as deduced by the exponential formula. Objections may be felt to this use of e_0 (here as throughout the subsequent tables) as a basis, since e_t involves e_0, which is an extrapolated value, certainly not exact, and possibly wide of the truth. Such a criticism is valid, but inasmuch as the values of e_0 employed are nearly equal, and as the percentage deviations are used merely for purposes of expressing relative accuracy, the possible

error involved is nearly annulled.   Hence, although it would be better to compute δt, and express this as a percentage of the absolute temperature τ, the added labor did not seem justified by the small gain.

The exponential equation applied to the Barus data yields

$$\Sigma_0^t e = 0.7691 \, \tau^{1.373} - 1730, \text{ or}$$
$$e_\tau = 0.7691 \, \tau^{1.373}, \text{ and } \beta = 1730 \text{ mv.}$$
$$\text{Range of data } 350° \text{ to } 1075° \text{ C.}$$

[N.B. This equation was deduced with the value $0° \text{C.} = 273°.7$ absolute, whereas in all subsequent tables $0° \text{C.} = 273°.0$ absolute is employed as a more probable value.   The numerical values of the constants are therefore subject to a slight modification, but as for the present purpose we are concerned only with δ, which would not be sensibly changed, the recomputation is not worth while.]

Columns six and seven, Table II., give δ and its percentage value for the exponential equation.

The Barus Equation. — The excessive labor involved in the evaluation of the constants P, Q, P', and Q' of Barus's proposed equation detracts so seriously from its usefulness that I have also allowed it to deter me from computing them for the above tabulated values.   The comparison of the values of δ for his " Equation 3," and for an approximate exponential of my own based on the same data, is, however, decidedly in favor of the latter.

The logarithmic equation applied to the Barus data yields

$$\Sigma_0^t e = 2.665 \, t^{1.220},$$

or its equivalent,

$$\log \Sigma_0^t e = 1.220 \log t + 0.42570.$$

The deviations are given in the last two columns of Table II.

Holborn and Wien Data. — This important comparison * of the rhodo-platinum thermo-couple with the porcelain bulb air thermometer up to high temperatures was performed under the auspices of the Reichsanstalt at Berlin, and appears to be on the whole the most important and reliable contribution to this subject in recent years.   The experimental work was evidently conducted with great care, and although not showing the concordance of results, nor the multiplication of observations of Barus's work, yet in respect to stem-exposure correction, to exposure of the thermal junction, and to direct measurement of the coefficient of expansion of the bulb, it is probably more

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* Holborn and Wien.   Zeit. f. Instk., XII. 257, 296 (1892).   Also in full in Wied. Ann., XLVII. 107 (1892).

free from systematic error. It is to be regretted that the results were not more thoroughly discussed, and that neither a chemical analysis nor even a statement was given to indicate the reliability of the stated percentage composition of the various alloys used. For when closely examined, the data seem to indicate a definite relation between the composition and the emf., as was shown by a relation discovered between the constants in my exponential equations for the various alloys. The deviations were only such as might be attributed to uncertainty of composition, but as no measure of the latter was given, a statement of the relations and interesting inferences from them is not warranted. It is also unfortunate that an analysis, or at least a definite statement of the percentage purity, was not given for the gold, copper, and silver whose melting points were observed. The assertion that the gold showed on qualitative analysis only a trace (" Spur ") of copper, and the silver a " trace " of iron, is hardly definite. The value of the whole work would have been enhanced by these additions far more than in proportion to the comparatively small labor demanded by them, and such completeness is naturally to be expected in work emanating from this source. It is to be hoped that a continuation of this research is in progress, and that additional high melting points may be measured.

Table III., columns one and two, quotes the interpolated mean values of several comparisons expressed in international microvolts and degrees centigrade. With regard to these data it should be stated that below about 400° they were not supposed to be of as high accuracy as above that point. Also, that, owing to unavoidable circumstances, the data below 300° were obtained with only a single air thermometer bulb, and similarly those above about 1300° with one bulb only, but a different one, while the data intermediate between 400° and 1300° are the mean of observations with the two bulbs. This fact may partially account for the erratic character of the residuals above 1300°, where the deviations are so great and so distributed (see diagram, page 212) as to render these observations of very little service. Direct comparison with the air thermometer was made with one 10 per cent rhodo-platinum couple " A " only.

The parabolic formula applied to these by Holborn and Wien, when corrected as to decimal points,* is

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* The equation at both references, and stated to be in microvolts and degrees, is erroneously printed as

$$" t = f(e) = 13.76\,e - 0.004841\,e^2 + 0.000001378\,e^3."$$

$$t = 1.376 \cdot 10^{-1} \, (\Sigma_0^t e) - 4.841 \cdot 10^{-6} \, (\Sigma_0^t e)^2 + 1.378 \cdot 10^{-10} (\Sigma_0^t e)^3.$$

$$\text{Range } -80° \text{ C. to } +1445° \text{ C.}$$

The residuals are given in Table III., columns three and four.

TABLE III.

HOLBORN AND WIEN.   AIR THERMOMETER COMPARISONS, ALLOY A.

t Centigr.	$\Sigma_0^t e$ mv.	H. and W. Eq.		Avenarius.		Exponential.		Logarithmic.	
		δ = Data − Eq. mv.	Per Cent = $100\frac{\delta}{e}$	δ = Data − Eq. mv.	Per Cent = $100\frac{\delta}{e}$	δ = Data − Eq. mv.	Per Cent = $100\frac{\delta}{e}$	δ = Data − Eq. mv.	Per Cent = $100\frac{\delta}{e}$
−80	−361	—		—		—		—	
0	0	0	0	0	0	0	0	0	0
+82	+500	−84	−4.6	−107	−5.1	−69	−3.6	+40	+2.20
154	1000	−147	−6.1	−166	−7.2	−122	−4.8	+11	+0.50
220	1500	−135	−5.0	−199	−7.1	−140	−4.7	−27	−1.00
273	2000	−150	−4.5	−142	−4.3	−85	−2.6	+16	+0.50
329	2500	−130	−3.6	−124	−3.3	−73	−1.9	+11	+0.30
379	3000	−60	−1.4	−66	−1.5	−24	−0.57	+45	+1.00
431	3500	−30	−0 60	−41	−0.90	−6	−0.12	+45	+0.90
482	4000	0	0.00	−14	−0.22	+8	+0.15	+41	+0.80
533	4500	+10	+0.17	−1	0	+9	+0.15	+27	+0.50
584	5000	0	0.00	0	0	−2	−0.03	+1	+0.01
633	5500	0	0.00	+9	+0.13	−4	−0.06	−13	−0.20
680	6000	+10	+0.11	+28	+0.38	+5	+0.07	−15	−0.20
725	6500	+30	+0.40	+58	+0.74	+26	+0.33	−1	−0.01
774	7000	−10	−0.12	+35	+0.42	−5	−0.06	−39	−0.47
816	7500	+20	+0.22	+78	+0.90	+33	+0 37	−8	−0.10
862	8000	0	0.00	+69	+0.74	+19	+0 20	−24	−0.26
906	8500	−20	−0.20	+72	+0.74	+19	+0.20	−25	−0.25
952	9000	−55	−0.55	+44	+0.43	−.10	−0.10	−53	−0.52
996	9500	−88	−0.80	+29	+0.26	−24	−0.22	−67	−0.60
1038	10000	−88	−0.80	+29	+0.25	−20	−0.18	−57	−0.50
1080	10500	−100	−0.85	+22	+0.20	−23	−0.20	−54	−0.43
1120	11000	−100	−0.80	+31	+0.25	−7	−0.06	−22	−0.19
1163	11500	−140	−1.10	−6	−0.05	−33	−0.26	−51	−0.40
1200	12000	−96	−0.74	+26	+0.20	+9	+0.07	+2	+0.02
1241	12500	−96	−0.70	0	0	−3	−0.03	−8	−0.06
1273	13000	0	0.00	+84	+0.60	+94	+0.67	+111	+0.80
1311	13500	+36	+0.24	+84	+0.57	+110	+0.80	+140	+0.90
1354	14000	+24	−0.17	+10	+0.07	+.58	+0.38	+107	+0.70
1402	14500	−60	−0.40	−141	−0.90	−65	−0.41	+2	+0.01·
1445	15000	−72	−0.45	−231	−1.40	−128	−0.80	−38	−0.23
ad. for 0 to 1445.		1.12		1.15		0.77		1.46	
ad. for 431 to 1445.		0.39		0.43		0.25		0.38	
ad. for 431 to 1241.		0.43		0.36		0.15		0.34	

The Avenarius Formula applied to the Holborn and Wien data with constants deduced from $t = 584°$ and $1273°$ becomes

$$\Sigma_0^t e = (t - t_0) \, \{7.2188 + 0.00\,229\,94 \, (t + t_0)\}, \text{ or}$$

$$= 7.2188 \, t + 2.2994 \cdot 10^{-3} \, t^2.$$

$$\text{Range } 0° \text{ to } 1445° \text{ C.}$$

The deviations in microvolts and percentages from this equation are given in columns five and six, Table III.

The exponential equation fitting these data most closely, and coinciding with them as nearly the same points as the others, viz., at about 584° and 1250°, is

$$\Sigma_0^t e = 0.57\ 674\ \tau^{1.377} - 1310,\ \text{or}$$

$$e = 0.57\ 674\ \tau^{1.377},\ \beta = 1310.$$

$$\text{Range } 0° \text{ to } 1445° \text{ C.}$$

The deviations in microvolts and percentages are in columns seven and eight, Table III.

The logarithmic equation applied to the Holborn and Wien data on A yields

$$\Sigma_0^t e = 2.1682\ t^{1.2156},\ \text{or}$$

$$\log \Sigma_0^t e = 1.2156 \log t + 0.36\ 610.$$

The deviations are given in the last two columns of Table III.

Holborn and Wien not only compared the ten per cent rhodo-platinum couple A directly with the air thermometer, but compared with A seven other couples in which one element was platinum, and the other a rhodo-platinum alloy, the percentage of rhodinum being stated respectively as, for C_1 and C_2, 10 per cent (these two I have combined under C), D, 9 per cent, E, 11 per cent, F, 20 per cent, G, 30 per cent, H, 40 per cent. For the present purpose I have combined these data, which were differences of emf. between C and A, D

TABLE IV.

Designation of the Alloy.	Nominal Percentage of Rhodium.	Expon. Eq. Constants.		
		m	n	β $mv.$
D	9	1.36 71	1.250	1517
C	10	0.95 596	1.310	1485
E	11	0.81 734	1.336	1469
A	10	0.57 689	1.377	1305
F	20	0.22 865	1.522	1167
G	30	0.06 599 0	1.708	956
H	40	0.06 303 4	1.720	977

and A, etc., with the corresponding emf. of A, and thence have deduced the exponential equations for each of the alloys. Table V. gives the percentage deviations of these alloys from the exponential equation (data — equation), and Table IV. shows the values of m, n, and β for those equations.

TABLE V.

HOLBORN AND WIEN. — COMPARISON OF ALLOYS.

t	D	A	C	E	F	G	H	Average.
°C. 154	—	—4.8	—	—4.0	—	—5.0	—4.4	—4.5
273	—0.9	—2.6	—2.7	—2.2	—2.3	—3.5	—2.3	—2.6
379	+2.1	—0.57	—0.80	—0.50	—1.3	—0.60	—0.25	—0.67
482	+2.6	+0.15	—0.03	0.	—0.60	+0.22	+0.46	—0.03
584	+0.9	—0.03	+0.19	+0.08	+0.13	+0.30	—0.03	+0.02
680	—0.30	+0.07	+0.13	+0.13	+0.12	—0.16	—0 26	0.
774	—0.19	—0.06	—0.08	—0.02	—0.12	—0.42	—0.46	—0.19
862	+0.23	+0.20	+0.20	+0.20	+0.09	+0.15	—0.11	+0.12
952	+0.20	—0.10	0.	—0.11	—0.15	+0.09	—0.24	—0.08
1038	+0.12	—0.18	—0.10	—0.21	—0.27	+0.04	—0.14	—0.16
1120	—0.15	—0.06	—0.09	—0.02	+0.10	+0 01	+0.22	—0.01
1200	+0.02	+0.07	0.	+0.10	0.	+0.04	0.	+0.03
1273	—	+0.67	+0.70	+0.80	+0.80	+0.43	+1.00	+0.73
1354	—	+0.38	+0.60	+0.67	+0.51	+0.30	+1.00	+0.58
1445	—	—0 80	—0.38	—0.50	—	—0.90	—0.40	—0.60
a. d. 400–1200	0.52	0.15	0.09	0.10	0.12	0.16	0.21	0.07
a. d. 400–1445	—	0.25	0.21	0.24	(0.24)	0.23	0.36	
		Direct from Air Th.						

*Chassagny and Abraham Data.** — The apparently very careful measurements of these observers cover a range of 0° to 100° C. with

* Chassagny et Abraham. Ann. de Chim. et de Phys., XXVII. 355 (1892).

observations at 25°, 50°, and 75° only. The range is too short, and the intervals are too great to render the work of much service in testing a general formula, but if its accuracy is as high as about 0°.01, as it appears to be, this in part offsets the disadvantage. Measurements of $\Sigma_0^t e$ and t were made with four thermo-couples with the results shown in Table VI. (international microvolts and degrees centigrade on hydrogen scale).

TABLE VI.

Couple.	$\Sigma_0^{100} e$	$\Sigma_0^{75} e$	$\Sigma_0^{50} e$	$\Sigma_0^{25} e$
Fe–Cu	1093.2	864.9	604.8	315.5
Fe–Pt Rh	895.1	708.9	496.1	259.1
Fe–Ag	1123.0	885.6	617.4	321.1
Fe–Pt	1685.1	1278.9	859.9	432.1

The Avenarius equation was applied to these data by Chassagny and Abraham in the form

$$\Sigma_0^t e = a\, t + b\, t^2.$$

They evaluated the constants from the 50° and 100° data. With these they computed the temperatures which the equation would yield by insertion of the observed values $\Sigma_0^{25} e$ and $\Sigma_0^{75} e$. These values are given in Table VII., columns two and three.

The exponential equation applied to these data for Fe – Pt becomes

$$\Sigma_0^t e = 105.096\ t^{0.7360} - 6525.3 \quad [\text{Range } 0° \text{ to } 100° \text{ C.}].$$

The values of t corresponding to the observed values $\Sigma_0^{25} e$ and $\Sigma_0^{75} e$ are given in Table VII. It has not seemed for the present purpose worth while to make similar computations for the other couples, as they would not materially affect the inferences to be drawn.

The logarithmic equation yields

$$\Sigma_0^t e = 19.2946\ t^{0.970595} ;$$
$$\log \Sigma_0^t e = 0.97\,059\,5 \log t + 1.28\,543\,6.$$

The deviations are given in the table.

TABLE VII.

Couple.	Avenarius.		Exponential.				Logarithmic	
	t	δt	t	δt	δ mv.	$100\,\delta/e$ Per Cent.	δt	δ mv.
Fe–Cu	24.88°	+0.12°	°	°			°	
Fe–Pt Rh	24.885	0.115						
Fe–Ag	24 87	0.13						
Fe–Pt	24.87	0.13	24.80	+0.20	−2.6	−0.037	+0.52	−6.7
Fe–Cu	75.13	−0.13						
Fe–Pt Rh	75.135	0.135						
Fe–Ag	75.135	0 135						
Fe–Pt	75.135	0.135	75.15	−0.15	+2.5	+0.032	−0.26	+4.3

The Noll Data. — A contribution of much permanent value to the data on thermo-electrics has recently been made by Noll,[*] who has measured $\Sigma_0^t e$ and t for thirty-two couples over a range in most cases of 0° C. to 218° C. The metals employed (including carbon) were usually of a high and stated degree of purity, and consisted of eighteen different substances, two of which were alloys (German silver and brass), and the remainder samples of different degrees of purity or hardness of the pure substances. The couples contained, as one element, for the most part, either copper or mercury. Temperatures were reduced to the air thermometer scale.

The Avenarius formula was applied to fourteen of the more important of them by Noll. The deviations are given in Table VIII.

The exponential equation I have applied to the same data. It has not seemed essential to reproduce here the entire series of data, and the deviations of both equations. They are, therefore, presented in a somewhat more digested form. Table VIII. gives the constants for the exponential equation (those for the Avenarius may be found in Noll's article), the mean deviations (= data — equation) for each series, and the mean percentage deviations (= 100 δ/e). (See remark as to use of e under " Barus Data.") Table IX. groups the percentage deviations under their nearest values of t for exhibiting their systematic

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[*] Noll, Wied. Ann., LIII. 874 (1894).

character. The fact that the experimental method brought the obser-
vations all very nearly to the respective temperatures t given in the
table renders this grouping possible. I have taken the liberty of
correcting a few obvious numerical errors, and of dropping a very
few values evidently containing a mistake.

TABLE VIII.

NOLL'S DATA ON PURE METALS.

Couple.	m	n	β mv.	Av. Pct. Deviation.	
				Avenarius.	Expon.
Au–Hg	$4.6954 \cdot 10-8$	2.136	750.4	± 0.27	± 0.17
Ag–Hg	$2.8637 \cdot 10-3$	2.206	677.8	0.33	0.15
Ni–Cu	$8.2333 \cdot 10-1$	1.511	3950.2	0.30	0.17
(Cd–Cu	$3.7617 \cdot 10-11$	4.94	40.7	0.48	3.40)
Br–Cu	$2.4969 \cdot 10-1$	1.366	531.1	0.14	0.13
Zn–Hg	$8.2890 \cdot 10-4$	2.420	651.6	0.15	0.18
Pb–Cu	$1.7674 \cdot 10-2$	1.800	429.0	0.05	0.07
Cu$_1$–Hg	$4.6726 \cdot 10-3$	2.130	768.4	0.12	0.11
[Fe–Hg	$1.0913 \cdot 10+2$	0.7220	6264.2]		
Co–Hg	$8.3295 \cdot 10-3$	2.166	1575.2	0.26	0.22
Pt$_1$–Cu	$2.1475 \cdot 10-8$	2.266	711.1	0.08	0.12
Pt$_2$–Cu	$1.1095 \cdot 10-8$	2.353	599.0	0.19	0.25
Sn$_1$–Cu	$4.2021 \cdot 10-2$	1.667	482.8	0.21	0.09
Mg–Cu	$2.0449 \cdot 10-2$	1.782	448.7	0.15	0.17
Al–Cu	$7.5643 \cdot 10-2$	1.590	565.3	0 11	0.12
G. s.–Cu	$2.0454 \cdot 10-1$	1.684	2589.9	0.06	0.05
Average omitting Cd–Cu and Fe–Hg				± 0.17	± 0.14

It may, perhaps, not be out of place here to caution those who
would make use of Noll's data to their full accuracy that his original,
and not his interpolated, numbers should be resorted to. The approxi-

mate linear interpolation which he has employed is not as accurate as his experimental data demand.

The logarithmic equation applied to the Cu–Hg couple as typical of the Noll data yields

$$\Sigma_0^t e = 2.57\ 434\ t^{1.2250};$$

or $$\log \Sigma_0^t e = 1.2250 \log t + 0.41\ 066\ 5.$$

The residuals to this expression are given in Table IX.

TABLE IX.

AVENARIUS EQUATION. — DATA MINUS EQUATION IN PER CENT.

	15°	57°	100°	138°	181°	198°	217°
Au–Hg	−0.10	−0.40	0	+0.05	+0.60	+0.90	0.
Ag–Hg	−0.13	+0.20	0	+0.21	−0.50	−1.30	0.
Ni–Cu	−0.26	−0.15	0	0.	−0.22	−0.31	−1.17
Br–Cu	—	−0.10	0	+0.20	+0.17	+0.35	0.
Zn–Hg	—	−0.03	0	+0.09	+0.41	+0.40	0.
Pb–Cu	—	−0.03	0	−0.11	+0.12	−0.04	0.
Cu_1–Hg	+0.02	−0.16	0	+0.01	+0.15	+0.38	0.
Co–Hg	—	—	0	+0.42	0.	—	−0.56
Pt_1–Cu	—	−0.12	0	−0.06	+0.09	+0.21	0.
Pt_2–Cu	—	−0.13	0	−0.11	0.	+0.67	−0.21
Sn_1–Cu	—	−0.20	0	0.	+0.34	+0.40	+0.30
Mg–Cu	—	+0.11	0	+0.22	−0.37	+0.11	0.
Al–Cu	—	+0.16	0	+0.18	−0.18	+0.15	0.
G. s.–Cu	—	−0.01	0	+0.16	+0.11	—	0.
Average	−0.12	−0.07	0	+0.09	+0.05	+0.16	−0.12

TABLE IX. — *Continued.*

EXPONENTIAL EQUATION. — DATA MINUS EQUATION IN PER CENT.

	15°	57°	100°	138°	181°	198°	217°
Au–Hg	+0.01	−0.12	−0.06	−0.06	+0.09	+0.12	−0.80
Ag–Hg	−0.18	+0.22	0.	+0.05	−0.03	0.	−0.50
Ni–Cu	−0.26	−0.16	0.	+0.07	0.00	0.	−0.72
Br–Cu	—	−0.06	−0.01	+0.12	+0.20	−0.26	−0.13
Zn–Hg	—	−0.30	+0.02	+0.14	+0.10	+0.65	−0.04
Pb–Cu	—	−0.10	0.	−0.25	+0.04	0.	0.00
Cu$_1$–Hg	−0.19	−0.27	+0.01	—	−0.03	0.	−0.25
Co–Hg	—	−0.05	+0.01	+0.48	−0.01	—	−1.00
Pt$_1$–Cu	—	−0.15	+0.03	−0.06	+0.17	0.	−0.31
Pt$_2$–Cu	—	−0.56	0.	−0.10	−0.16	+0.70	0.
Sn$_1$–Cu	—	−0.04	+0.04	−0.29	+0.12	+0.06	0.
Mg–Cu	—	+0.18	0.	+0.15	−0.52	+0.17	0.
Al–Cu	—	+0.16	0.	+0.12	−0.24	+0.18	0.
G. s.–Cu	—	+0.07	−0.01	+0.08	—	—	+0.05
Average	−0.16	+0.08	+0.01	+0.03	−0.02	+0.14	−0.27

LOGARITHMIC EQUATION. — DATA MINUS EQUATION IN PER CENT.

	15°	57°	100°	138°	181°	198°	217°
Cu$_1$–Hg	+2.3	+1.5	0.	−0.40	0.	+0.50	+0.80

DISCUSSION OF THE DEVIATIONS.

Plots are given in the following diagram with temperatures as abscissas and percentage deviations between the data and the sundry equations as ordinates, i. e. 100 δ/e where δ = data-equation. Inspection will show that with one exception (viz. the logarithmic equation applied to the Barus data) these plots, whether the equation is the ordinary parabolic, the Avenarius, the Barus, the exponential, or the logarithmic, have the same general form, which may be imperfectly

dsecribed as follows.   If the equation be made to conform to the data
at 0°C. and at two higher points, a and b, then the deviation will be of
the negative sign from 0 to a, positive from a to b, and negative above b.
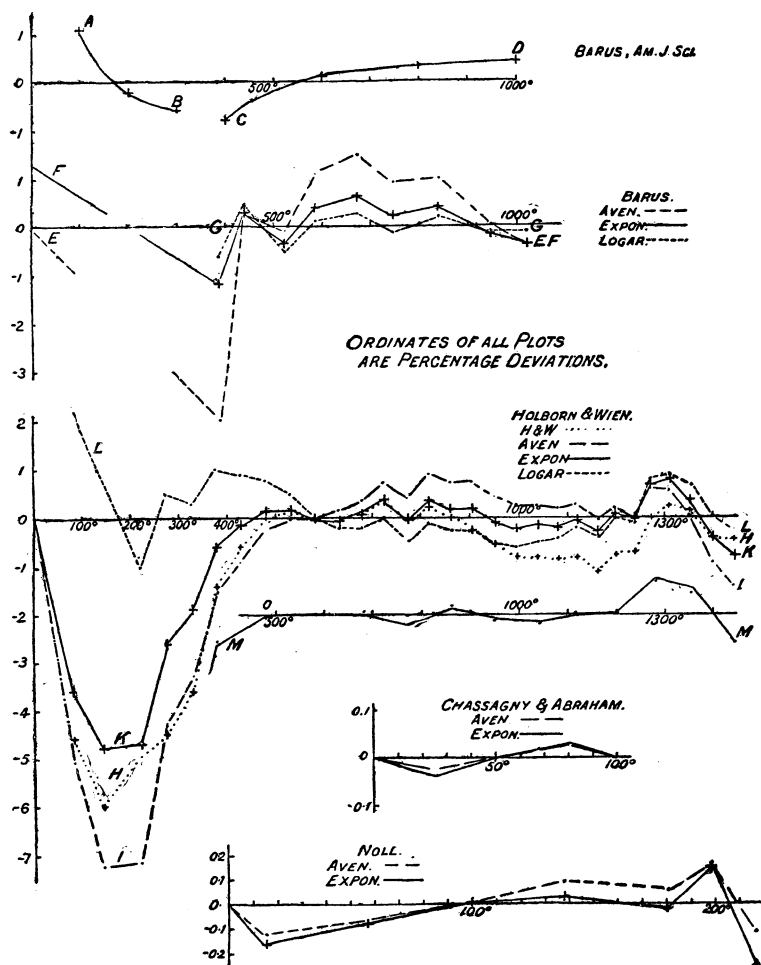
The slight departures from this general form are clearly due either to
accidental errors, or to failure to make the equation conform to the
data at all three points, or at suitable ones.   The evidence is there-
fore conclusive that *for all of the expressions the deviations are sys-
tematic and not purely " accidental" in character.*

One of two inferences is therefore warranted : —

1. *That neither the parabolic, Avenarius, Barus, exponential, nor logarithmic equation is the natural expression of the function.*

2. Or that the scale of temperature to which the values of t are referred in the foregoing investigations departs from the normal scale by an amount and system roughly indicated by the above residual plots.

The latter inference, suggested by Chassagny and Abraham in the interpretation of their results, does not seem to possess much weight, notwithstanding the urgent need of renewed elaborate experimental investigation of the relation between the hydrogen, air, and thermo-dynamic scales of temperature.

As to the relative usefulness of the various expressions for purposes of interpolation and extrapolation some further inspection is necessary. The Barus equation 3, line CD, shows slightly smaller deviations on the plot than do the Avenarius and exponential, lines EE and FF. This, however, is due to the fact that the data against which 3 is tested are mean interpolated values, and hence have a sensibly less variable error than those against which the other equations are tested. An approximate exponential equation showed less deviations than 3 against the same data. There seems, therefore, to be no advantage in this equation sufficient to offset the difficulty of evaluation of its constants.

Applied to the Barus data from 350° to 1250°, the exponential equation shows deviations considerably less than one half as great as those of the Avenarius, while those of the logarithmic equation are so small as to lie far within the range of the variable errors, and they moreover show no clear evidence of systematic error between these limits of temperature. *For interpolation in the Barus data, therefore, the logarithmic equation is far preferable*, and must be conceded to be representative of the data. *For extrapolation* it is undoubtedly better than the Avenarius, which (as would the exponential in less degree) would certainly give above 1000° extrapolated values of Σe too large, or of t too small. The advantage due to its simplicity is also to be noted.

Applied to the Holborn and Wien data from 400° to 1450° the exponential equation shows (line KK) the same sort of superiority to both logarithmic (line LL) and Avenarius (line II) that the logarithmic shows to the others with the Barus data, but in a still more marked degree. Within the limits 450° to 1450°, in fact, the distribution of the residuals to the exponential is such as not to warrant

of itself alone any inference of systematic departure, especially when the mean line MM from all the couples is considered. It will be noted as an important confirmation of both the exactness of the electrical measurements in the investigation and the applicability of the exponential formula through a considerable range of alloys (and therefore of values of m and n) that this mean line MM is almost identical in form with the line KK for alloy A. Relatively to the Holborn and Wien formula (line HH), the exponential possesses a similar advantage, with also the merit of greater simplicity of form.

It may therefore be affirmed that *for interpolation between* 450° *and* 1450° *in the H. and W. data the exponential equation is abundantly exact.* *For extrapolation* above 1450° it would not be entirely safe, although presumably better than the others, since the departure between 0° and 450°, and the similarity of the form to others, makes a systematic departure sufficiently certain.

Applied to the Chassagny and Abraham data, 0°–100°, and to the Noll data, 0°–218°, (see diagram,) the Avenarius and exponential formulæ show about equal deviations, but with the advantage slightly on the side of the former. In the case of the Noll data, the line indicates that the systematic error is slightly greater for the exponential than for the Avenarius expression. The average deviations in Table IX., on the contrary, show that for each individual equation the concordance is greater for the exponential than the Avenarius. This discrepancy is due to the fact that, in order to eliminate local accidental errors, the equations (both Avenarius and exponential) are not all made to coincide with the data at the same temperatures, so that the process of averaging by which the data for the Noll plots is obtained is not numerically rigid. This does not, however, sensibly affect the general form of the curve. The greater ease of computation of the numerical constants of the Avenarius expression, and its applicability where both t and t_0 change, ought not to be overlooked. For extrapolation the exponential would be safer, for the reason that it has been above shown that for long ranges its systematic error is less.

The logarithmic equation fits the Noll data very badly, as shown by the deviation in Table IX. (not plotted), and also is much less close to the Chassagny and Abraham data than are the others.

THE GENERAL CONCLUSION as to applicability, then, seems to be that, while the *Avenarius* expression may be equally good or better than the exponential *for interpolation over short ranges,* yet *for inter-*

*polation over long ranges and for extrapolation above the observation
limits the exponential is decidedly preferable.* The exponential form
is also preferable to the remaining expressions with the exception
noted.

The logarithmic form, although closely applicable to the Barus data,
is of more doubtful general value, yet on account of its great con-
venience it may find application in industrial pyrometry, as will be
elsewhere indicated. Although failing below 300° or 400°, it may
probably be applied to the irido- or rhodo-platinum couple between
400° and 1200° C. with a maximum error not exceeding about 5°.
If extended to cover 400° to 2000° the error might rise to 15° or 20°.

More in detail it may be briefly noted by way of summary : —

That the logarithmic equation fits the Barus data between 400°
and 1250° with scarcely sensible systematic error, and within the
limits of variable errors of the data.

That the exponential equation similarly fits the Holborn and Wien
data within the limits 400° to 1445°.

That when made to coincide with the data at about 450° and 1200°
the systematic deviations of the exponential equation from the Barus
data, and of the logarithmic equation from the Holborn and Wien
data, are in general of opposite sign and of roughly equal magnitude.

BARUS MELTING AND BOILING POINT DATA.

From the foregoing demonstration of its applicability, it seems
proper to apply the logarithmic formula to the Barus thermo-electric
data on melting points.*

Whether the extrapolation above 1000° by the logarithmic formula
is entitled to any great weight may be questioned, but there is no
obvious reason why it is not more reliable than by any of the others.
I have employed the equation given on page 202, which repre-
sents very closely Barus's high temperature air thermometer com-
parisons, calculating thence the temperatures t corresponding to the
values of $\Sigma_{20}^{t} e$ given by Barus for the various points, assuming Barus's
value $\Sigma_{0}^{26} e = 150$ mv. The results are given in column three of
Table X. Column four quotes the most reliable previous determina-
tions of the same points by other observers. As to which of the two
columns of results best represents Barus's work there can be little
doubt from the above evidence that below 1000° it is the second, that

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* Amer. Jour. Sci., XLVIII. 332 (1894).

is, the one computed from the logarithmic equation. These combine both his own air thermometer and melting point work. Above 1000^c the logarithmic values are probably slightly too high.

TABLE X.

BARUS MELTING AND BOILING POINTS.

	Computed by Eq. 3.	Computed by Log. Eq.	Data by other Observers.	
Mercury (B. Pt.)	$\overset{\circ}{357}$	$\overset{\circ}{359}$	$\overset{\circ}{356}.76$	Callendar and Griffiths.
Zinc	420	423	417.57	" "
Sulphur (B. Pt.) .	446	449	444.53	" "
Aluminum . . .	638	641	635	Le Chatelier.
Selenium (B. Pt.)	694	697		
Cadmium (B. Pt.)	782	782		
Zinc (B. Pt.) . .	929	926	930	Deville and Troost.
Silver	986	985	968	Holborn and Wien.
			954	Violle.
Gold	1091	1090	1072	Holborn and Wien.
			1035	Violle.
Copper	1096	1095	1082	Holborn and Wien.
			1054	Violle.
Bismuth . . .	1435	1441		
Nickel	1476	1485	1450	Carnelly and Williams.
Palladium . . .	1585	1597	1500	Violle.
Platinum . . .	1757	1783	1775	Violle.

REMARK.

Review of the laborious researches which have been devoted to the direct comparison of thermo-electric elements with the air thermometer, mainly for the purpose of advancing the art of pyrometry, has enforced the conviction that, at least for the immediate future, this end would be better served by accurate gas thermometer meas-

urements of melting points of metals. Each such determination made upon a reproducible metal of known high purity under proper reproducible conditions fixes an enduring and reproducible reference point, a pyrometric " bench mark." And there are enough inexpensive metals, together with a possible system of simple alloys, to give points of sufficient frequency. These would then afford a convenient means of obtaining accurately known high temperatures for purposes of study of all high temperature phenomena, and particularly for calibrating thermo-electric, electrical resistance, optical, or other secondary pyrometric interpolation apparatus, — for it must be remembered that all such apparatus is necessarily secondary, the gas thermometer being inevitably the primary.

On the other hand, comparison with the air thermometer of a thermo-couple, or of a resistance pyrometer, or the study of any progressive thermal phenomenon, while it possibly may result in the eduction of a natural law, is very unlikely to lead to anything more than the establishment of an approximate equation with constants characteristic only of the individual materials actually employed, and not transferable to other, although similar materials. Such results are obviously of a much more ephemeral character than the melting point measurements. Even when any pyrometer thus tested is applied to the establishment of melting points, it must at best yield results inferior to direct application of the gas thermometer, except in cases where the latter is hampered by want of sufficient quantity of the metal to be experimented upon, — a condition which need only affect such costly substances as gold and platinum.

Stated broadly, the great need of the art of pyrometry is convenient methods of producing, or of recognizing when produced, a series of accurately known high temperatures. The analogous problem has been partially solved for thermometry at temperatures up to 300° C. by the investigation of boiling points of certain chemically pure substances under controlled pressures.

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, September, 1895.